

(54) COMPOSITE MATERIAL PROVIDED WITH HYDROPHILIC SURFACE

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a composite material in which the surface which is made hydrophilic in accordance with photoexcitation of a photocatalytic semiconductor material exhibits good hydrophilic properties-holding properties for a long period of time even when it is kept under an indoor weak illumination or in a dark place.

SOLUTION: A composite material consists of a layer comprized of a base material and a photocatalytic semiconductor formed on the surface of the base material, and a hydrophilic layer formed on the surface and consisting of a silicone resin, etc., wherein at least a part of org. groups bonded to silica or silicon atom is replaced, with hydroxy group and in which the surface of the hydrophilic layer is made hydrophilic in accordance with photoexcitation of a photocatalytic semiconductor material.

CLAIMS

[Claim 1] It is the composite which consists of a base material, a layer which consists of a light catalytic semi-conductor formed in the front face of said base material, and a layer of the hydrophilic property further formed in the front face, and is characterized by carrying out hydrophilization of the front face of the layer of said hydrophilic property according to optical pumping of said light catalytic semiconductor material.

[Claim 2] The layer of said hydrophilic property is composite according to claim 1 characterized by a part of silica and/or organic radical [at-least] combined with the silicon atom being silicone resin permuted by the hydroxyl group.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates the front face of a base material to an advanced hydrophilic property at nothing and the technique to maintain. This invention relates to the antifog technique of preventing the cloudiness of a base material, and waterdrop formation, in more detail by carrying out hydrophilization of the front face of a mirror, a lens, and the transparence base material of sheet glass and others to altitude. This invention relates to the technique which prevents that a front face becomes dirty, carries out self-consecration (self-cleaning) of the front face, or is cleaned easily again by carrying out hydrophilization of the front face of a building, a windowpane, a machinery, or an article to altitude.

[0002]

[Description of the Prior Art] If hydrophilization of the base material front face is carried out, since adhesion waterdrop will come to spread uniformly on a base material front face, the cloudiness of glass, a lens, and a mirror can be prevented effectively and it is useful to the devitrification prevention by hygroscopic moisture, the field-of-view nature reservation in case of rainy weather, etc. Since a rainfall and rinsing can drop easily even if hydrophobic pollutants, such as products of combustion, such as carbon black contained in exhaust gas, such as city dust and an automobile, fats and oils, and a sealant leached moiety, cannot adhere easily and adhere further if hydrophilization of the base material front face is carried out, it is convenient.

[0003] In the field of an antifog coating and a sheathing antifouling paint, hydrophilic resin is proposed from the former especially from such a situation (for example, JP,5-68006,U, a "macromolecule", 44 volumes and the May, 1995 issue, p.307). Moreover, the surface treatment approach for carrying out hydrophilization is also proposed (for example, JP,3-129357,U).

[0004] However, the hydrophilic resin by which the conventional proposal is made is converted into a contact angle with water, and hydrophilization is carried out only to 30-50 degrees, and it cannot demonstrate sufficient cloudy prevention effectiveness.

Moreover, adhesion of the pollutant which consists of inorganic argillaceous one and a rainfall, and the detergency by rinsing are not enough. And even if hydrophilization is carried out temporarily, the condition is unmaintainable over a long period of time.

Moreover, by the surface-preparation approach (etching processing, plasma treatment) to make [which carries out hydrophilization] the conventional proposal, even if it can carry out hydrophilization to altitude temporarily, the condition is unmaintainable for a long period of time.

[0005] Then, when the light catalytic semi-conductor layer was formed in the base material front face, this invention person invented the technique in which hydrophilization of the layer front face was carried out to altitude, according to optical pumping of a light catalytic semiconductor material, and proposed that it could use for dirt prevention of the front face of the antifog technique and building which prevent the cloudiness of a base material, and waterdrop formation, a windowpane, a machinery, or an article, self-consecration (self-cleaning), and ***** (PCT/JP 96/No. 00733). Since according to this approach it converts into a contact angle with water and hydrophilization is carried out to altitude to 10-degree or less extent, sufficient cloudy prevention effectiveness is demonstrated and adhesion of the pollutant which consists of inorganic argillaceous one and a rainfall, and the detergency by rinsing also improve by leaps and bounds. Moreover, according to optical pumping of a light catalytic semiconductor material, the condition that hydrophilization of the front face was carried out is maintained and recovered.

[0006]

[Problem(s) to be Solved by the Invention] However, in having formed in the base material front face the layer which consists only of a light catalytic semi-conductor, once carrying out hydrophilization according to optical pumping of a light catalytic semiconductor material, when it is left in a dark place, lifting of a contact angle with water is quick. Therefore, if the light of wavelength which is made to excite a light catalytic semi-conductor and deals in it frequently was not irradiated, the hydrophilic property on the front face of a base material could not be maintained, but there was a

problem that the cloudiness of a base material, the tightness of waterdrop formation, a building, a windowpane, a machinery or the dirt tightness of the front face of an article, self-consecration nature, and ease to clean were not demonstrated. So, in this invention, when hydrophilization is once carried out according to optical pumping of a light catalytic semiconductor material, it aims at offering the composite which presents hydrophilic maintenance nature with a good rear spring supporter to a long period of time in the bottom of indoor feeble lighting, or a dark place.

[0007]

[Means for Solving the Problem] In this invention, it consists of a layer which consists of a light catalytic semi-conductor formed in the front face of a base material and said base material that the above-mentioned technical problem should be solved, and a layer of the hydrophilic property further formed in the front face, and the composite characterized by carrying out hydrophilization of the front face of the layer of said hydrophilic property according to optical pumping of said light catalytic semiconductor material is offered. It is made for the layer of said hydrophilic property to be silicone resin with which a part of silica and/or organic radical [at least] combined with the silicon atom were permuted by the hydroxyl group in the desirable mode of this invention. When hydrophilization is once carried out according to optical pumping of a light catalytic semiconductor material by preparing the layer which consists of the above-mentioned matter in the front face of the layer which consists of a light catalytic semi-conductor, a composite front face comes to present hydrophilic maintenance nature with a good rear spring supporter to a long period of time in the bottom of indoor feeble lighting, or a dark place.

[0008]

[The mode of implementation of invention] The component of this invention is explained below. Here, when using it for a base material for the object of antifog, field-of-view reservation, and devitrification prevention, if it is the base material of the transparency of a mirror, a lens, glass, prism, a transparent plastic, etc., either can be used for it. When using it for dirt tightness, self-consecration nature, and the ease to clean object, a ceramic, others, for example, a metal, plastics, a tree, a stone, cement, concrete and the paint plate that are those combination, a laminate, etc. can be used. [above]

[0009] Hydrophilization here means change in the condition that water wettability improves. For example, even if hydrophobic pollutants, such as products of combustion, such as carbon black contained in exhaust gas, such as city soot dust, and excretions from the exhaust port of a building, an automobile, fats and oils, and a sealant leached moiety, cannot adhere easily and adhere, in order to enable it to drop simply by the rainfall or rinsing, a base material front face is good to convert into a contact angle with water and to carry out hydrophilization of the 50 degrees or less to 30-degree or less extent more preferably. Even if an inorganic argillaceous pollutant cannot adhere easily and furthermore adheres, in order to enable it to drop simply by the rainfall or rinsing, a base material front face is good to convert into a contact angle with water and to carry out hydrophilization of the 10 degrees or less to 5-degree or less extent more preferably. Moreover, in order to spread uniformly the waterdrop adhering to a transparence base material front face, to prevent the cloudiness of glass, a lens, a mirror, etc. effectively and to aim at the devitrification prevention by hygroscopic moisture, and the field-of-view nature reservation in case of rainy weather, a base material front face is good to convert into a contact angle with water and to carry out hydrophilization to 10-degree or less.

extent.

[0010] A light catalytic semi-conductor here means the ingredient which can carry out hydrophilization of the front face highly by giving a polarity to ***** probably and forming a water-of-adsorption layer by the reaction through the electron hole or conduction electron generated by optical pumping of the electron in a valence band, and, more specifically, anatase mold titanium oxide, a rutile type titanium dioxide, tin oxide, a zinc oxide, bismuth(III) oxide, a tungstic trioxide, ferric oxide, strontium titanate, etc. can be used.

[0011] Inorganic oxides, such as a silica, an alumina, and tin oxide, and the silicone resin with which a part of organic radical [at least] combined with the silicon atom was permuted by the hydroxyl group can use for the construction material of the layer of the hydrophilic property formed in a composite maximum front face suitably. 100nm or less of 50nm or less of thickness of the layer of a hydrophilic property is more preferably set to 20nm or less here. If it does in this way, since the probability which the electron hole or conduction electron generated by optical pumping of a light catalytic semi-conductor diffuses to a front face is securable to some extent, the hydrophilization reaction by optical pumping of a light catalytic semi-conductor can be promoted. If the layer of a hydrophilic property is formed by the matter with a refractive index lower than a light catalytic semi-conductor, the layer of a hydrophilic property can serve as an antireflection film further. here, with the matter with a refractive index lower than a light catalytic semi-conductor, when for example, a light catalytic semi-conductor is anatase mold titanium oxide (refractive index 2.5), the silicone resin (said -- 1.4-1.6) with which a part of a silica (said -- 1.5), alumina (said -- 1.6), tin oxide (said -- 1.9), and organic radical [at least] combined with the silicon atom were permuted by the hydroxyl group can use suitably.

[0012] Here, the silicone resin with which a part of organic radical [at least] combined with the silicon atom was permuted by the hydroxyl group contacts a light catalytic semi-conductor to silicone resin, and can be produced by approaches, such as the approach of carrying out optical pumping of the light catalytic semi-conductor, corona discharge treatment, plasma treatment, and alkali treatment. Here, silicone resin points to the resin formed of hydrolysis of the film-forming material containing at least one sort of organoalkoxysilane, its hydrolyzate, and its dehydration condensation polymerization object, and dehydration condensation polymerization. As organoalkoxysilane, here, for example Methyl trimetoxysilane, Ethyl trimethoxysilane, phenyl trimethoxysilane, n-propyltrimethoxysilane, Methyl triethoxysilane, ethyltriethoxysilane, phenyl triethoxysilane, n-propyl triethoxysilane, a methyl triisopropoxy silane, An ethyl triisopropoxy silane, a phenyl triisopropoxy silane, n-propyl triisopropoxy silane, MECHIRUTORI t-butoxysilane, ECHIRUTORI t-butoxysilane, FENIRUTORI t-butoxysilane, n-pro PIRUTORI t-butoxysilane, dimethyl dimethoxysilane, Diethyl dimethoxysilane, phenylmethyl dimethoxysilane, diphenyl dimethoxysilane, n-propylmethyl dimethoxysilane, dimethyl diethoxysilane, Diethyl diethoxysilane, phenylmethyl diethoxysilane, n-propylmethyl diethoxysilane, Dimethyl diisopropoxysilane, diethyl diisopropoxysilane, Phenylmethyl diisopropoxysilane, n-propylmethyl diisopropoxysilane, JIMECHIRUJI t-butoxysilane, JIECHIRUJI t-butoxysilane, phenyl MECHIRUJI t-butoxysilane, n-propyl MECHIRUJI t-butoxysilane, beta-(3, 4-epoxycyclohexyl) ethyl trimethoxysilane, etc. can use those mixture.

[0013] Optical pumping of a light catalytic semi-conductor is performed by irradiating the light which has bigger energy (namely, short wavelength) than the energy gap between the conduction electron band of a light catalytic semiconducting crystal, and a valence band. When a light catalytic semi-conductor is anatase mold titanium oxide, more specifically, 387nm or less and the light which has [in the case of a rutile type titanium dioxide] the wavelength of 344nm or less in the case of 413nm or less and tin oxide are irradiated. The light source which guided indoor lighting like a fluorescent lamp, an incandescent lamp, a metal halide lamp, and a mercury lamp, sunlight, and those light sources with the fiber of low loss as the light source can be used. In order to carry out hydrophilization of the base material front face by optical pumping of a light catalytic semi-conductor, with [the illuminance of the above-mentioned excitation light] two [or more / 0.01mW //cm], it is more preferably enough two or more 0.001 mW/cm.

[0014] The approach of forming in a base material front face the layer which consists of a light catalytic semi-conductor, and forming the layer of a hydrophilic property in the front face further is divided roughly, and has two approaches below.

(1) When the matter which forms especially the layer of a hydrophilic property is an ingredient with specific gravity smaller than a light catalytic semi-conductor, or when it is amorphous materials, produce the liquefied mixture of a light catalytic semi-conductor particle (or the precursor) and the matter (or the precursor) which forms the layer of a hydrophilic property, and apply and heat-treat on a base material front face.

(2) Cover a base material front face with the matter which forms the layer of a hydrophilic property for said covering surface further after a coat by the light catalytic semi-conductor particle.

[0015] In the approach of the above (1), with the matter which forms the layer of the hydrophilic property which consists of an ingredient with specific gravity smaller than a light catalytic semi-conductor, when for example, a light catalytic semi-conductor is titanium oxide, the silicone resin with which a part of silica and organic radical [at least] combined with the silicon atom were permuted by the hydroxyl group is mentioned. In the approach of the above (1), with the matter which forms the layer of the hydrophilic property which consists of amorphous materials, when for example, a light catalytic semi-conductor is titanium oxide, the silicone resin with which a part of organic radical [at least] combined with a silica, titania-silica glass, silica-alumina glass, silica-lithium glass, and a silicon atom was permuted by the hydroxyl group is mentioned.

[0016] In the approach of the above (1), with the precursor of a light catalytic semi-conductor, when for example, a light catalytic semi-conductor is crystalline titanium oxide, the non-fixed form titanium oxide which will be crystalized if it calcinates, the hydroxylation titanium which will form non-fixed form titanium oxide if dehydration condensation polymerization is carried out, the titanium alkoxide (for example, tetra-ethoxy titanium, tetraisopropoxy titanium, tetra-n-propoxytitanium, tetrabutoxytitanium, tetramethoxy titanium) which will form hydroxylation titanium if it hydrolyzes, a titanium chelate, titanium acetate, a titanium tetrachloride, sulfuric-acid titanium, etc. can use suitably.

[0017] Next, the process of the above (2) is explained below taking the case of the case where the matter with which a light catalytic semi-conductor forms the layer of crystalline titanium oxide and a hydrophilic property is a silica. First, a base material front face is covered with a light catalytic semi-conductor particle. There are the

following approaches among the approaches.

(1) Form a non-fixed form titanium oxide layer on a base material, and make it crystallize by baking.

****** Apply mixture to them on the surface of a base material, and make them dry it with the coating method of spray coating, flow coating, spin coating, DIP coating, roll coating, and others, after advancing [or] hydrolysis in a titanium alkoxide, a titanium chelate, and titanium acetate thoroughly, adding hydrolysis inhibitors, such as a hydrochloric acid and ethylamine, and diluents, such as ethanol and propanol, and advancing hydrolysis selectively. By desiccation, hydrolysis completes, hydroxylation titanium generates, and a non-fixed form titanium oxide layer is formed of the dehydration condensation polymerization of hydroxylation titanium. The obtained non-fixed form titanium oxide layer is calcinated and crystallized above 400 degrees C.

****** If needed, after adding an alkali water solution, with the coating method of spray coating, flow coating, spin coating, DIP coating, roll coating, and others, apply to the aqueous acids of a titanium tetrachloride and sulfuric-acid titanium on the surface of a base material, and dry them. By desiccation, hydrolysis completes, hydroxylation titanium generates, and a non-fixed form titanium oxide layer is formed of the dehydration condensation polymerization of hydroxylation titanium. The obtained non-fixed form titanium oxide layer is calcinated and crystallized above 400 degrees C.

****** Put a non-fixed form titanium oxide layer on a base material front face by irradiating an electron beam by the oxidizing atmosphere at the target of titanium metal or titanium oxide. The obtained non-fixed form titanium oxide layer is calcinated and crystallized above 400 degrees C.

(2) With the coating method of spray coating, flow coating, spin coating, DIP coating, roll coating, and others, apply a crystalline titanium oxide sol on the surface of a base material, and dry it.

[0018] Next, the example of an approach which forms the layer of a hydrophilic property in the front face further is explained taking the case of the case where the matter which forms the layer of a hydrophilic property is a non-fixed form silica.

****** tetra-alkoxysilane (for example, a tetra-ethoxy silane and tetra-isopropoxysilane --) In tetra-n-propoxysilane, tetra-butoxysilane, a tetramethoxy silane, a silicon chelate, and silicon acetate, hydrolysis inhibitors, such as a hydrochloric acid and ethylamine, Adding diluents, such as ethanol and propanol, and advancing hydrolysis selectively Or after advancing hydrolysis thoroughly, with the coating method of spray coating, flow coating, spin coating, DIP coating, roll coating, and others, mixture is applied on the surface of a base material, and is dried. By desiccation, hydrolysis completes, a silanol generates and a silica layer is formed of the dehydration condensation polymerization of a silanol.

****** Put a silica layer on a base material front face by irradiating an electron beam by the oxidizing atmosphere at metal silicon or the target of a silica.

****** With the coating method of spray coating, flow coating, spin coating, DIP coating, roll coating, and others, apply a silica sol on the surface of a base material, and dry it.

[0019]

[Example]

Example 1 (a mixing method, AES analysis)

First, in order to graduate a substrate front face to the aluminum substrate of 10cm angle, it covered with the silicone layer beforehand. For this reason, the aluminum substrate (#1

sample) which mixed a silica sol (the Japan Synthetic Rubber make, GURASUKA A liquid) and trimethoxysilane (the Japan Synthetic Rubber make, GURASUKA B liquid) so that it might be set to 3:1 by the weight ratio, applied this mixed liquor to the aluminum substrate, was stiffened at the temperature of 150 degrees C, and was covered with the base coat of silicone of 3 micrometers of thickness was obtained. Next, the thin film which consists of a light catalytic semi-conductor and silicone resin was formed in #1 sample front face. The anatase mold titanium oxide sol 56 weight section (the product made from the Nissan chemistry, TA-15) and said silica sol 33 weight section were mixed in more detail, by ethanol, after dilution, further, the above-mentioned trimethoxysilane 11 weight section was added, and the constituent for titanium oxide content silicone coatings was prepared. Applied this constituent for coatings to the front face of #1 sample, it was made to harden at the temperature of 150 degrees C, the topcoat layer of 0.1 micrometers of thickness which consists of an anatase mold titanium oxide particle and silicone resin was formed, and #2 sample was obtained. The sum total weight section of a silica and silicone resin is set to 1 to the anatase mold titanium oxide particle 1 weight section by the presentation of the topcoat layer of #2 sample here.

[0020] # About two samples, ultimate analysis of the direction of a cross section was performed by the Auger-analysis method. A result is shown in drawing 1 (a) - drawing 1 (c). Drawing 1 (a) shows the elemental-analysis result of a sample maximum front face. Ti was not observed, although Si, C, N, and O were observed in the sample maximum front face so that drawing 1 (a) might show. Since Ti was not observed, it is thought that the anatase mold titanium oxide which is a light catalytic semi-conductor does not exist in a sample maximum front face. On the other hand, Si, C, and O were observed because silicone existed in the maximum front face. Since the dispersion liquid of a titanium oxide sol were a nitric acid and the nitrogen of the nitric-acid origin was observed, it is thought of that N was furthermore observed. Drawing 1 (b) shows the elemental-analysis result of 20nm lower layer side from the sample maximum front face. In this cross section, Ti besides Si, C, N, and O was accepted so that drawing 1 (b) might show. Since Ti was observed, a sample maximum front face shows that the anatase mold titanium oxide which is a light catalytic semi-conductor exists at 20nm lower layer. Moreover, silicone also exists in this cross section from Si, C, and O having been observed simultaneously. Drawing 1 (c) shows the elemental-analysis result of 200nm lower layer side, i.e., the cross section in a base coat, from the sample maximum front face. As drawing 1 (c) shows, in this cross section, it turns out that Si, C, and O are accepted and it consists only of silicone. It was checked that the composite which consists of a layer (silicone layer by which anatase mold titanium oxide was distributed) which consists of a light catalytic semi-conductor joined to the front face of a base material and said base material by the above-mentioned process, and a layer (silicone layer) further formed in the front face is formed from the above thing.

[0021] Next, the ultraviolet-rays light source (the product made from the Sankyo electrical and electric equipment, black light blue (BLB) fluorescent lamp) of 20W was used for #2 sample, ultraviolet rays were irradiated with the ultraviolet-rays illuminance of 0.5 mw/cm² on the 1st, and #3 sample was obtained. # About three samples, the contact angle with the water on the front face of a sample was measured using the contact angle measuring instrument (the product made from consonance surface chemistry, CA-X150). After the contact angle trickled waterdrop into the sample front face from the

micro syringe, it was measured after 30 seconds. Consequently, to the contact angle with water having been 85 degrees, according to optical pumping of a light catalytic semiconductor, it converted into the contact angle with water, and hydrophilization was carried out to 2 degrees by #3 sample by #2 sample.

[0022] Next, #3 sample was moved to the dark place and a change of a contact angle with subsequent water with time was investigated. Consequently, after 3 degrees and two weeks, after 5 degrees and three weeks, 7 degrees and one month after, it went up only to 7 degrees, but it was checked also in the dark place at the long period of time after one week that the hydrophilic property of rear-spring-supporter altitude is maintained.

[0023] Example 2 (the silica applying method)

The non-fixed form silica layer was first formed on the glass substrate. The tetra-ethoxy silane (COL coat company make, ethyl 28) was applied on the glass substrate with the spray coating method, and, more specifically, it calcinated at 300 degrees C for 20 minutes. Next, #4 sample which performed sputtering in the oxygen ambient atmosphere by having used titanium oxide as the target, and formed the non-fixed form titanium oxide layer on the non-fixed form silica layer was obtained. By furthermore calcinating #4 sample at 500 degrees C, #5 sample which non-fixed form titanium oxide was crystalized and changed to the anatase mold titanium oxide layer was obtained. The thickness of #5 sample was 50nm here. # #6 sample by which the silica layer was formed in 5 sample front face on the front face by calcinating after spreading the tetra-ethoxy silane solution (0.9 % of the weight of concentration) further diluted with the ethanol solvent at 150 degrees C by the flow coating method for 20 minutes was obtained. The thickness of a surface silica layer is equivalent to about 50nm here. On the other hand, #7 sample by which the silica layer was formed in #5 sample front face on the front face by calcinating after spreading the tetra-ethoxy silane solution (0.09 % of the weight of concentration) further diluted with the ethanol solvent at 150 degrees C by the flow coating method for 20 minutes was obtained. The thickness of a surface silica layer is considered to be 10nm or less here.

[0024] # When the sunlight exposure was performed outdoors for one week, about 5 - #7 sample, hydrophilization of the contact angle with water was carried out for the contact angle with water to altitude by each by 10 degrees by 0 degree and #6 sample by #5 sample and #7 sample. Next, when #5 by which hydrophilization was carried out to above-mentioned altitude - #7 sample was moved to the dark place and left for one week, to the contact angle with water having gone up to 40 degrees by #5 sample which does not form the surface silica layer, by #6 sample in which the surface silica layer was formed, it stopped at the contact angle with 25-degree water, and the comparatively low contact angle was maintained by 15 degrees and #7 sample.

[0025]

[Effect of the Invention]. Even if the composite front face which carried out hydrophilization according to optical pumping of said light catalytic semiconductor material is left in the bottom of indoor feeble lighting, or a dark place, it comes to present hydrophilic maintenance nature with a good rear spring supporter to a long period of time by forming the layer of the hydrophilic property which a part of silica or organic radical [at least] combined with the silicon atom becomes from the silicone resin permuted by the hydroxyl group in the front face of the layer which consists of a light catalytic semiconductor formed on the surface of the base material.